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Surfactant-Assisted Synthesis and Characterization of Novel Chain-Like CoNi Alloy Assemblies

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Novel chain-like CoNi alloy assemblies with a length of up to 6–7 μm were successfully prepared by a surfactant-assisted hydrothermal synthetic route at 100 °C for 2 h. The individual submicrospheres built from smaller CoNi nanoparticles had a diameter of about 400–500 nm. These microspheres were then integrated to form the novel chain-like CoNi alloy assemblies. The effects of synthetic parameters such as surfactant and solvent on the formation and morphology of CoNi samples were investigated. The experimental results showed that $N_2H_4{\cdot}H_2O$ and CTA^+ play important roles in the formation of the novel chain-like CoNi alloy assemblies. Based on the structural information provided by X-ray powder diffraction, scanning electron microscopy, transmission electron microscopy, selected-area electron diffraction and energy-dispersive X-ray analysis, a growth mechanism was tentatively proposed for the formation of chain-like CoNi alloy assemblies. Magnetic hysteresis measurement revealed that the chain-like CoNi alloy assemblies display ferromagnetic behavior with a saturation magnetization of 96.15 emu/g and a coercivity of 144.75 Oe at room temperature.

Introduction

Transition metal nanoparticles, especially those of Fe, Co and Ni, are considered to be very important for technological applications, such as electronic, optical and mechanic devices, magnetism, catalysis, superconductors and ferrofluids etc.[1–5] It is claimed by Ung et al.[6] that, as far as magnetic storage is concerned, very high storage density requires high magnetic anisotropy to overcome thermal effects and to prevent superparamagnetic behavior. Several kinds of magnetic anisotropy can be considered to meet this requirement, including (a) shape anisotropy of elongated magnetic particles, such as rods and wires;[7] (b) magnetocrystalline anisotropy (for example: CoPt, FePt, CuNi, $FeNi_3$, etc.);[8–12] and (c) exchange anisotropy of ferromagnetic/antiferromagnetic core-shell particles.[13]

As important transition metal alloys, CoNi alloys have been widely used for decoration, corrosion resistance and magnetic recording devices, etc.[14–17] Therefore, much effort has been made in preparation of CoNi alloys. Micro- and nanosized CoNi alloy particles were prepared by electrochemical reduction,[18–20] thermal decomposition of organometallic precursors,[21] sol-gel routes,[22] polyols of metal salts[23] and leaching technology.[24] Nanosized amorphous CoNi alloy powders were also obtained by sonochemical decomposition methods.[25] Using the cationic water-in-oil (W/O) microemulsion of water/butanol/cetyltrimethyl bromide (CTAB)/*n*-octane, Zheng and co-workers synthesized CoNi needle-like alloys of different compositions with aspect ratios of 10–20.[26] Zhang and co-workers fabricated CoNi nanowires within nanochannel alumina (NCA) templates.[27] The magnetic behavior of the nanowires showed strong temperature dependence. Furthermore, Ung et al. synthesized CoNi nanowires by heterogeneous nucleation in liquid polyol.[6] In our previous work, we reported the synthesis of submicro-sized spherical ferromagnetic CoNi alloy particles by a polyol process assisted by solvothermal treatment.[28] However, chain-like CoNi alloy assemblies have received much less attention, although they are (i) members of the family of one-dimensional structural materials, which are likely to play a critical role in the improvement of the efficiencies of various devices based on single particles or their composites and (ii) are of considerable interest in fundamental research since they provide a direct bridge between nanometer-scale objects and the macroscale world.[29]

Herein, we report the preparation of high-density chain-like CoNi assemblies by a surfactant-assisted hydrothermal method and characterize the size, structure and composition of the resultant particles by transmission electron microscopy, selected-area electron diffraction, scanning electron microscopy, energy-dispersive X-ray analysis and X-ray powder diffraction.

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Results and Discussion

The phase and purity of the as-prepared product formed at 100 °C for 2 h was determined by X-ray diffraction (XRD), as shown in Figure 1 for 2θ angle values of 20–80°. The feature peaks of the as-prepared arise at $2\theta = 44.44$, 51.72 and 76.32°, which match the (111), (200) and (220) characteristics of a face-centered cubic (fcc) structure, respectively. No characteristic peaks due to the impurities of $NiCl_2$, $CoCl_2$ or NaCl were detected, indicating that the as-obtained product was pure. In addition, there were no observable peaks in the XRD spectra corresponding to those of pure cobalt and nickel. If the homogeneous solid solution of CoNi were not formed, XRD peaks of pure Co or Ni should be observed simultaneously in the spectrum. These facts confirm that Co and Ni formed an alloy, rather than separate grains.

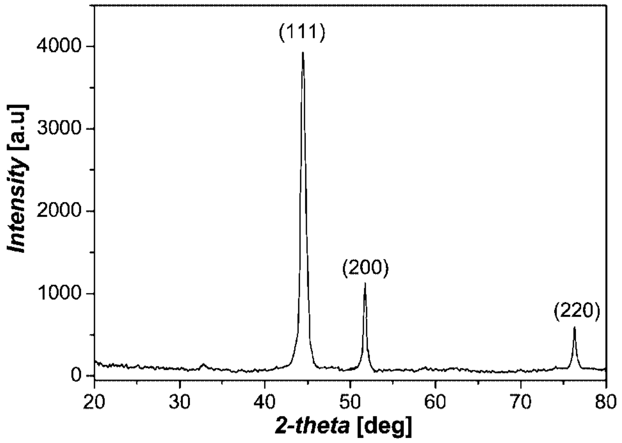

Figure 1. XRD pattern of the as-prepared sample obtained at 100 °C for 2 h.

Figure 2(a)–(c) shows SEM images of the as-synthesized product formed at 100 °C for 2 h. Figure 2(a) is the overall morphology of the sample, which indicates that the obtained product consists of large-scale chain-like assemblies. The magnified SEM image as shown in Figure 2(b) clearly displays that all of the CoNi chains are in the size range of 400–500 nm and in close contact with each other, forming branched, necklace-like chains with lengths of 6–7 μm. A close observation, as shown in Figure 2(c), reveals that the surface of the individual CoNi alloy submicroparticle is quite rough, and it presents a fine hierarchical nanostructure. On the basis of the above results, we conclude that the rough surfaces of these submicrospheres in the chain-like CoNi alloy assemblies are formed by attachment of nanoparticles, which may be related to the natural property and the presence of a surfactant. The morphology of the as-synthesized product was further determined by TEM as shown in Figure 2(d), which is consistent with that observed by SEM. The corresponding electron-diffraction pattern, displaying considerably sharp ring-like features of the selected area of the sample [Figure 2(e)], indicates that the as-obtained product is polycrystalline. The as-prepared alloy compositions were determined by EDX analysis under N_2. Figure 2(f) shows EDX spectra taken from the as-prepared products. The only detectable elements by EDX are cobalt and nickel, and the corresponding elemental analysis reveals that the atomic ratio of Co/Ni in the alloys is up to 1.0 which is very close to the designed composition, and hence the reduction reaction should be rather complete.

To investigate the influence of the surfactant on the formation feature of chain-like CoNi alloy assemblies, a synthetic experiment without CTAB was carried out. No chain-like materials that appeared in the experiment with the surfactant were observed [Figure 3(a)]. In addition, in the presence of CTAC, a similar result [Figure 3(b)] was obtained as in the presence of CTAB. These suggested that CTA^+ is a prerequisite to form the chain-like CoNi alloy assemblies. Other synthetic parameters were also examined. It was found that by introducing glycol into the present

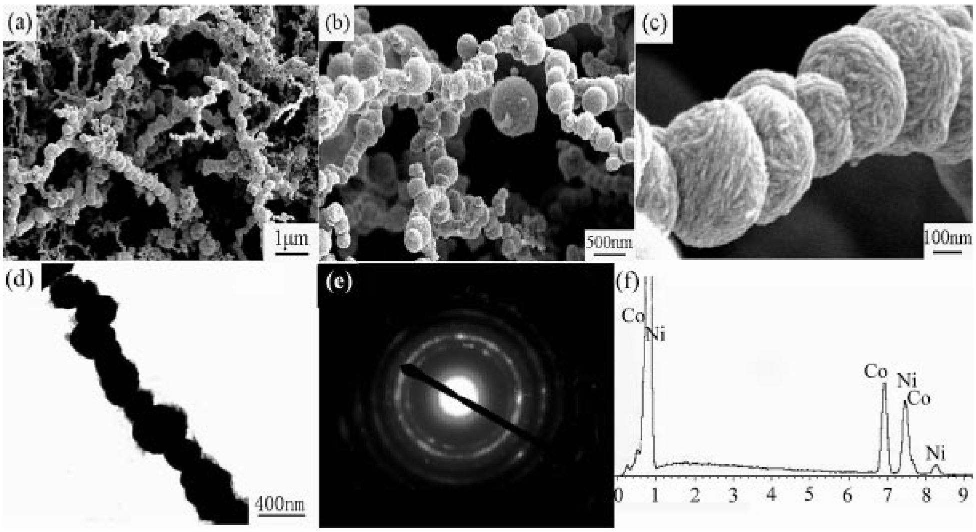

Figure 2. (a), (b), (c) SEM images at different magnifications of the as-prepared product. (d) TEM image, (e) the corresponding SAED pattern, (f) EDX spectrum of the as-prepared sample.

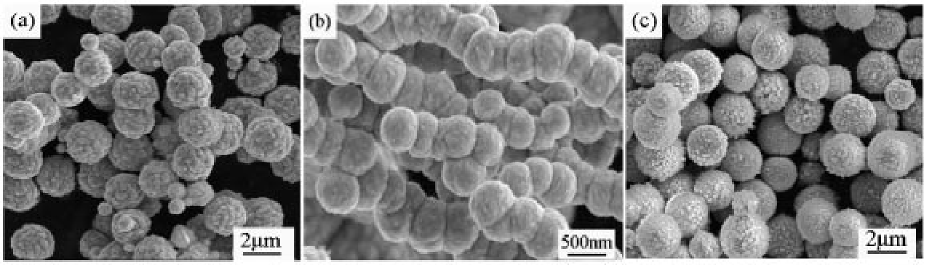

Figure 3. SEM images of the as-prepared product. (a) CoNi microspheres in the absence of surfactant. (b) CoNi submicrospheres in the presence of CTAC. (c) CoNi microspheres in the present system, with a water/polyol ratio of 1:2 (v/v).

system with a water/polyol ratio of 1:2 (v/v), CoNi microspheres rather than chain-like assemblies were obtained [Figure 3(c)]. Furthermore, the temperature rise did not show any additional effect on the morphology of the final products.

Regarding the mechanism for the growth of highly branched CoNi chain-like assemblies, we believe that both $N_2H_4{\cdot}H_2O$ and CTA^+ play important roles. In the experiment, hydrazine hydrate and sodium hydroxide were chosen as the reductant and buffer agent, respectively. The cobalt and nickel salts were reduced by hydrazine hydrate in concentrated basic media. The solution was blue before being reduced and afterwards became colorless. The reactions can be expressed as Equations (1) and (2).

$$2\,Ni^{2+} + N_2H_4 + 4\,OH^- \rightarrow 2\,Ni + N_2\uparrow + 4\,H_2O \quad (1)$$

$$2\,Co^{2+} + N_2H_4 + 4\,OH^- \rightarrow 2\,Co + N_2\uparrow + 4\,H_2O \quad (2)$$

Metallic cobalt and nickel give an intermetallic phase Equation (3).

$$Ni + Co \rightarrow CoNi \quad (3)$$

During the course of the reaction, the reduction of cobalt and nickel ions is effectively achieved by N_2H_4, which is a potent reducing agent in alkali solution.[12] A possible formation mechanism of chain-like CoNi alloy assemblies is proposed, as shown in Figure 4. Initially, cobalt(II) and nickel(II) ions react with hydroxy ions in the solution to form an intermediate phase consisting of cobalt and nickel hydroxide. Then, the redissolution of the intermediate solid phase takes place and the reduction of Co^{II} and Ni^{II} occurs according to Equations (1) and (2) and primary nuclei [Figure 4(a)] are formed in the presence of CTAB [see Equation (3)]. With the increase of the reaction time, presumably, the small CoNi primary nuclei diffuse and aggregate to form larger CoNi submicrospheres with a hierarchical nanostructure [Figure 4(b)] due to the magnetic dipole–dipole interaction[30] and effects of the CTA^+ templates. The larger CoNi submicrospheres are then assembled into chain-like assembles with multiple branches [Figure 4(e)] because of the stronger anisotropic magnetic forces.[31] This process is possible only when the magnetization of the particle does not fluctuate during the time of magnetic interaction in the suspension.[30] On the basis of the proposed mechanism for the growth of 1D nanostructure under the confinement of a capping reagent,[32,33] the surfactants CTAB or CTAC were necessary in the present procedure for the synthesis of chain-like CoNi alloy assemblies. It is assumed that the surfactants CTAB or CTAC play roles in at least two aspects. CTAB or CTAC are cationic surfactants, which can form CTA^+ in the solution. On the one hand, the surfactant could act as a template, which forms a CH_3–CH_2–CH_2–N chain-like structure;[34,35] on the other hand, it could form a shell surrounding the particles to prevent them from aggregating to larger particles during the reduction process of the intermediate solid phase. Though

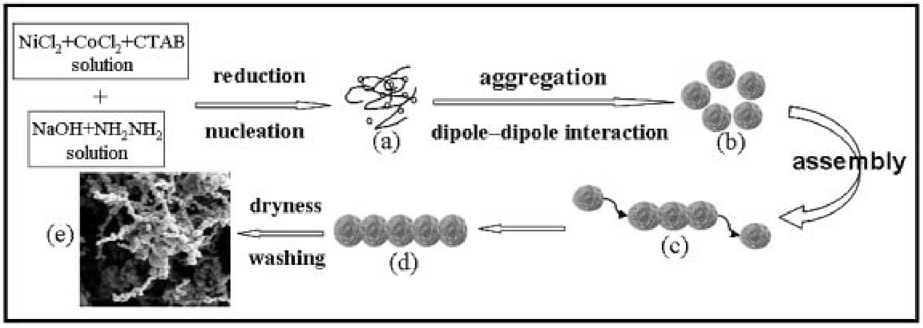

Figure 4. Schematic illustration of the formation and shape evolution of the CoNi alloy chain in the whole synthetic process: (a) Dissociative CTA^+ and CoNi primary nuclei, (b) CoNi submicrospheres with hierarchical nanostructure, (c) assembly of CTA^+ and CoNi alloy into a chain-like structure, (d) part of CTA^+ and CoNi alloy chain-like assemblies. (e) Removal of surfactant molecules to form chain-like CoNi alloy assemblies.

cobalt and nickel are easily oxidized, some possible oxides such as CoO, Co_2O_3 or NiO were not observed from the phase analysis by XRD. This might be due to the fact that the reaction was carried out at appropriate pH, temperature and hydrazine concentration and created under inert N_2 which does not favor cobalt and nickel oxidation.

The magnetic hysteresis measurement of the CoNi alloy was carried out at room temperature in an applied magnetic field sweeping from –10 to 10 kOe. Figure 5 shows magnetic hysteresis curves of the as-synthesized samples carried out at room temperature. The hysteresis loop of CoNi alloy samples reveals a ferromagnetic behaviour with a saturation magnetization (M_s) of 96.15 emu/g and a coercivity (H_c) of 144.75 Oe. Compared with the spherical CoNi alloy powders with a similar size of 200–500 nm in diameter in our previous work,[28] the coercivity increased from 108.23 to 144.75 Oe; on the other hand, the saturation magnetization decreased from 123.21 to 96.15 emu/g. It is well known that the size, structure and shapes of magnetic particles have effects on the magnetic properties of the products. The shape of the M/H curve, or the shape of the hysteresis loop, may be strongly affected not only by the specific particle surface area but also by the magnetic anisotropy.[36] The magnetic anisotropy includes magnetocrystalline anisotropy, shape anisotropy, stress anisotropy, induced anisotropy and exchange anisotropy.[36] Cullity has given an expression for the magnetostatic energy E_{ms} of the magnetic materials in the shape of a prolate spheroid with semimajor axis c and semiminor axes of equal length a as in Equation (4),[36] where M is the level of magnetization of an applied field, θ is the angle of the applied field to c, N_a and N_c are demagnetizing coefficients along a and c, respectively.

$$E_{ms} = 1/2M^2N_c + 1/2(N_a - N_c)M^2\sin^2\theta \qquad (4)$$

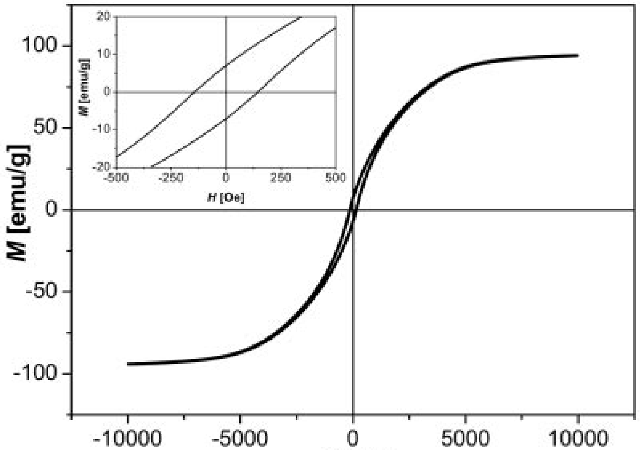

Figure 5. Hysteresis loop for the sample at room temperature.

The shape-anisotropy constant K_s is given by Equation (5).

$$K_s = 1/2(N_a - N_c)M^2 \qquad (5)$$

As Equation (5) shows, the strength of the shape anisotropy depends on the axial ratio c/a of the specimen. Symmetrically shaped nanoparticles, such as spheres, do not have any net shape anisotropy. However, the synthesized representative chain-like CoNi alloy assemblies with an aspect ratio of about 15 on average would have shape anisotropy, which should increase the coercivity. So, the different coercivity may be attributed to the shape anisotropy of chain-like CoNi alloy assemblies, which prevent them from magnetizing in directions other than along their easy magnetic axes,[37] hence leading to the different saturation magnetization and coercivity.

Conclusions

Novel chain-like CoNi alloy assemblies have been successfully prepared by the surfactant-assisted hydrothermal method. XRD, SEM, EDX, TEM, SAED, and VSM analyses have been employed for the characterization of the as-synthesized chain-like CoNi alloy assemblies. The results showed that CTA^+ plays an important role in the formation of chain-like CoNi alloy assemblies. The hysteresis loop of CoNi alloy samples revealed ferromagnetic behaviors with a saturation magnetization of 96.15 emu/g and a coercivity of 144.75 Oe at room temperature. A possible formation mechanism of the as-synthesized chain-like assemblies was proposed.

Experimental Section

All reagents were of analytical grade from Beijing Chemical Reagent Ltd. and used without further purification. In a typical experiment, 0.50 g of $CoCl_2·6H_2O$, 0.50 g of $NiCl_2·6H_2O$, and 1 g of cetyltrimethylamonium bromide (CTAB) were dissolved in 30 mL of deionized water, and the mixture was strongly stirred for 5 min; then ultrasound sonication was applied for 30 min to ensure that all the reagents were dispersed homogeneously in the solution. Afterwards, a certain amount of a hydrazine hydrate ($N_2H_4·H_2O$) solution in sodium hydroxide (NaOH) was added dropwise to the mixture whilst stirring. The obtained blue latex was then transferred into a 50 mL Teflon-lined stainless steel autoclave, sealed and maintained at 100 °C for 2 h after strongly stirring for 10 min. After being cooled to room temperature, the precipitates were collected and washed with deionized water and ethanol for several times. Finally, the precipitates were dried in vacuo at 40 °C for 12 h. The phase purity of the products was examined by X-ray powder diffraction (XRD) using a Rigaku D/max 2500 diffractometer at a voltage of 40 kV and a current of 200 mA with Cu-K_α radiation (λ = 1.5406 Å), employing a scanning rate of 0.02°/s in the 2θ range from 10 to 80°. Scanning electron microscopy (SEM) images and energy-dispersive X-ray (EDX) analysis were obtained using a HITACHI S-4300 microscope. Transmission electron microscopy (TEM) images and the corresponding selected-area electron-diffraction (SAED) pattern were taken with a HITACHI-600 transmission electron microscope at an accelerating voltage of 200 kV. Magnetic measurements for the samples were carried out at room temperature using a vibrating sample magnetometer (VSM, Lakeshore 7307, USA) with a maximum magnetic field of 10 kOe.

Acknowledgments

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